

# First-principles study of band structures of anthracene and tetracene under pressure



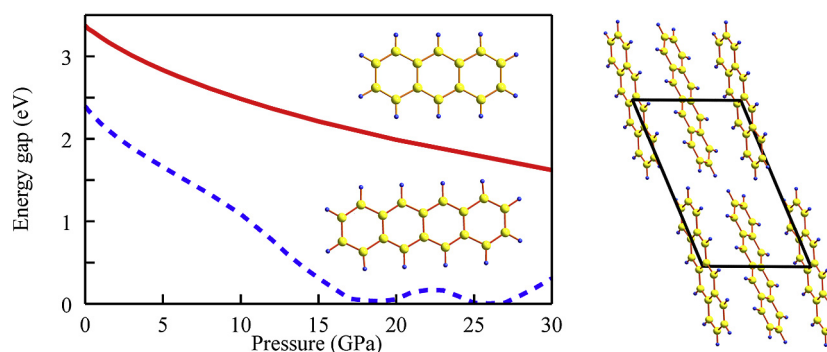
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## HIGHLIGHTS

- Hydrostatic pressure effects on lattice parameters and characteristic angles of anthracene and tetracene.
- Hydrostatic pressure effects on band structure of anthracene and tetracene.
- Transition from semiconductor to gapless semiconductor.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The pressure effect up to 30 GPa on the structural and electronic properties of crystalline anthracene and tetracene were studied within the framework of density functional theory with van der Waals interactions. Lattice parameters, bulk modulus and cohesive energy were calculated. The pressure dependence of interplanar angles, which describe the relative packing of molecules in the crystal, has been calculated. The calculated electronic band structures demonstrate the dependence of energy gap under pressure. Energy gap in crystalline anthracene monotonously decreases with increasing pressure. The tetracene energy gap decrease from 2.39 to ~0 eV at 26 GPa. Further increase of pressure subsequently increases energy gap.

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## 1. Introduction

Linear hydrocarbons are convenient model objects, the study of their properties gives a more thorough understanding of fundamental characteristics of molecular crystals. Flexibility is one of the important properties of organic electronics, that is why the study of linear hydrocarbons can be found in a large number of works [1–7].

Further progress in this field will contribute to creation of new electronic devices. Currently there are many review articles, for example, Wang et al. present a detailed review of organic electronics and prospects of its application [1]. New compounds have interesting characteristics, for example, the possibility to create luminescent organic semiconductors [8].

It has earlier been shown that DFT allows for correct description of crystal behavior both in ambient conditions and under pressure [9–15]. The dispersion interaction is very important for the formation of molecular crystals. Since correlated motion and many-

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body effects are the cause of the dispersion interaction, it is not taken into consideration in the standard approximations of DFT [16]. Increased unit cell volume and zero or negative value of cohesive energy are the result of structure optimization without taking into consideration the dispersion interaction. Despite weak dispersion interaction, it also plays a key role in the field of low pressures. Various algorithms have recently been suggested, as a result this interaction is now possible to include into existing DFT schemes [17]. The more detailed information on different schemes is contained in Refs. [18–22].

Today there is a number experimental and theoretical investigations on the properties of oligocenes. Ozlet et al. studied the effect of high pressure on structural properties of oligocenes using diamond anvil cells [23–25]. They investigated changes in length of lattice parameters, as well as the arrangement of molecules relative to each other in the crystalline anthracene and tetracene. Hummer et al. [2] studied the band structure of anthracene and tetracene at ambient conditions. Electronic structure of linear and polycyclic hydrocarbons was investigated by Fedorov et al. [26–28]. Ambrosch-Draxl et al. [3] conducted study of the electronic band structures as well as the optical spectra. Tkatchenko et al. [4] studied the pressure effect on energy gap of oligocenes. The main purpose of this work is to study pressure effect on electronic band structures and relative packing of molecules in anthracene and tetracene.

The molecules of anthracene and tetracene consist of three and four benzene rings, respectively. Isolated molecules have the same symmetry group  $D_{2h}$ , and they also have inversion center. In a crystal the symmetry group of molecules is  $C_{2v}$ . The anthracene and tetracene molecule in a crystal contains an inversion center. At the normal conditions the anthracene unit cell has the monoclinic space group  $P2_1/c$  [29], tetracene – triclinic  $P\bar{1}$  [30]. The tetracene unit cell is shown in Fig. 1. The anthracene and tetracene molecules in the crystals are shown in Fig. 1. The angle  $\theta$  is the herringbone angle between the two inequivalent molecules. The angle between the long molecular axes of two inequivalent molecules is labelled  $\delta$ .

## 2. Computational details

A plane-wave pseudopotential approach within DFT was used to calculate total energy. The PWscf program [31], which is incorporated into Quantum ESPRESSO (QE) [32] suite of electronic structure programs with the functional of Perdew, Burke, and Ernzerhof (PBE) [33], was used to carry out the computations. The ultrasoft pseudopotentials of the Rabe-Rape-Kaxiras-Joannopoulos type were used for calculations [34]. The crystal structures were optimized with the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method [35]. Monkhorst-Pack scheme [36] was used for the Brillouin zone sampling. The kinetic energy cutoff and the  $\mathbf{k}$ -points ensured the convergence of total energies. The energy cutoff equals 55 Ry. The  $\mathbf{k}$ -point grid is  $2 \times 4 \times 3$  and  $3 \times 4 \times 3$  for anthracene and tetracene, respectively.

Geometry relaxation was completed when all components of all forces are smaller than  $0.1 \text{ mRy (a.u.)}^{-1}$ . As the starting point structural data [29,30] were used. Besides, the computations were carried out with the CRYSTAL14 [37], using the PBE0 hybrid functional [38]. Thus, electronic band structures for the optimized structures were calculated within PBE0 hybrid functional. All calculations were performed by using standard 6-31G\* basis set [39]. Structural data, computed by QE, were used as the entry data. Other options for the computations were not changed.

I used a DFT-D [40]. In this scheme the empirical potential was added to the exchange–correlation potential and the total energy is given by

$$E_{\text{DFT-D}} = E_{\text{KS-DFT}} + E_{\text{disp}} \quad (1)$$

where  $E_{\text{KS-DFT}}$  is the Kohn–Sham energy and  $E_{\text{disp}}$  is a dispersion correction [41]. The QE and CRYSTAL14 include the DFT-D2 scheme [42]. In this paper performed computations within the DFT-D3(BJ) [43–47]. The dispersion energy is

$$E_{\text{disp}} = -\frac{1}{2} \sum_{A \neq B} s_6 \frac{C_6^{AB}}{R_{AB}^6 + [f(R_{AB}^0)]^6} + s_8 \frac{C_8^{AB}}{R_{AB}^8 + [f(R_{AB}^0)]^8}, \quad (2)$$

with

$$f(R_{AB}^0) = a_1 R_{AB}^0 + a_2, \quad (3)$$

$$R_{AB}^0 = \sqrt{\frac{C_8^{AB}}{C_6^{AB}}}. \quad (4)$$

Here, the sum is over all atom pairs in the crystal. The  $C_6$  and  $C_8$  are isotropic dispersion coefficients for atom pair AB, and  $R_{AB}$  – internuclear distance. The  $s_6$  and  $s_8$  are functional dependent scaling factors. Detailed information and values of all parameters can be found in the original works [27,43,44,47].

The lattice energy is given by

$$E_{\text{lat}} = E_{\text{mol}} - \frac{1}{n} E_{\text{bulk}} \quad (5)$$

where  $E_{\text{mol}}$  and  $E_{\text{bulk}}$  are the molecule and bulk crystal total energies, respectively, and  $n$  is the number of molecules per unit cell. Thus, the lattice energy is positive for any stable crystal.

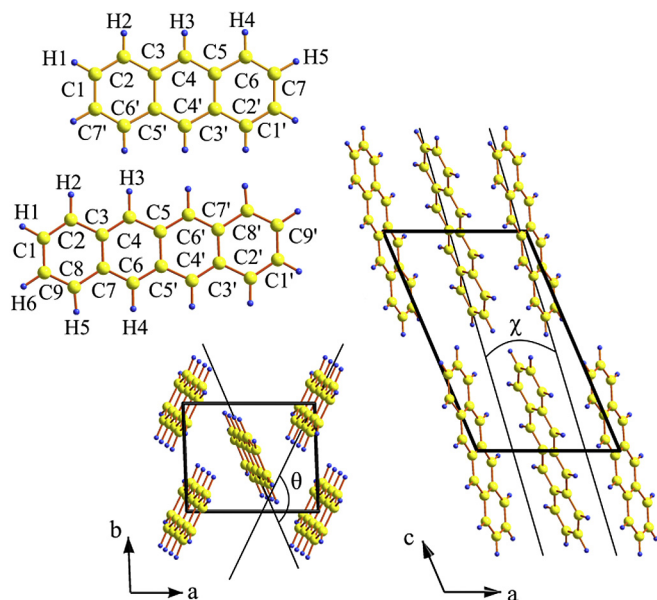


Fig. 1. The anthracene and tetracene molecule in the crystal. The two orientation angles of the molecules as they are used within this paper, illustrated for tetracene.

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